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Dual Stimuli-Responsive Interconvertible Heteroleptic Platinum Coordination Modes**

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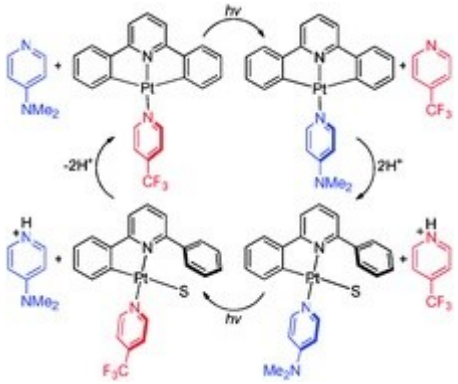
Supporting information:
[†]Electronic Supplementary Information (ESI) available: Synthesis and characterisation of all new compounds, details of all irradiative and non-irradiative ligand exchange experiments. See http://dx.doi.org/10.1039/C0CC01668C

Graphical abstract:



Abstract

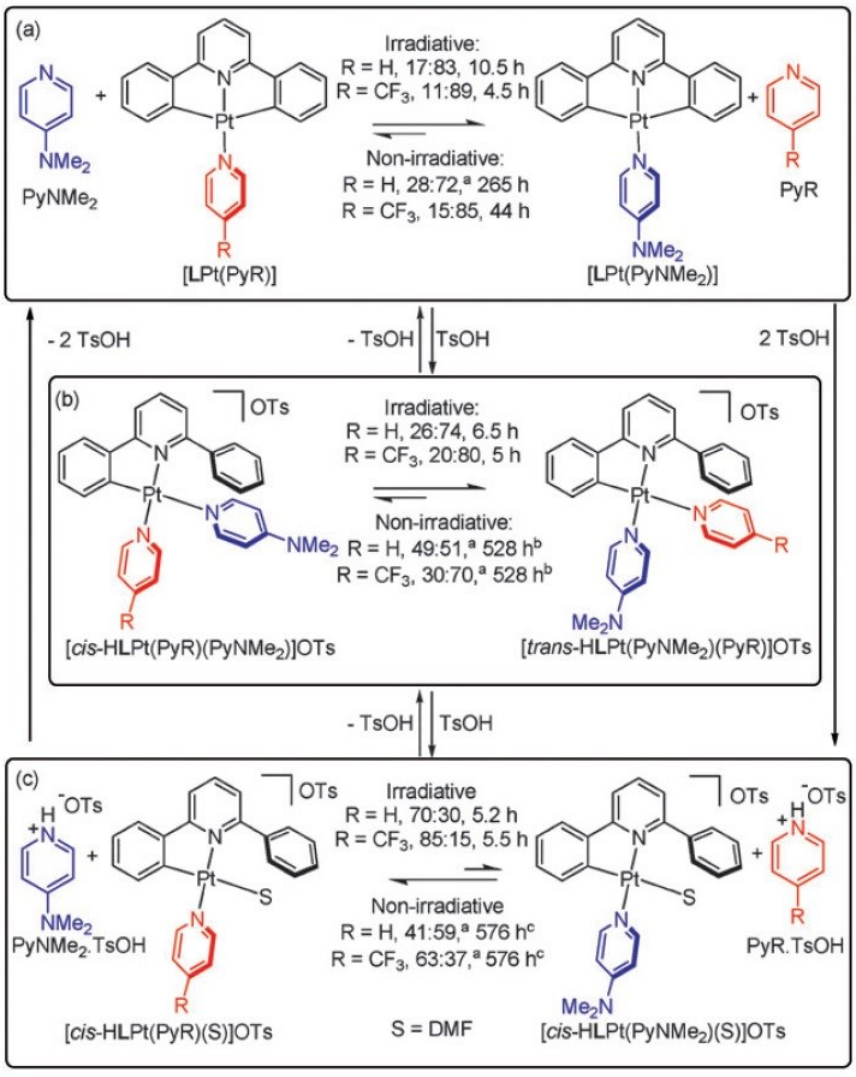
The exchange between different equilibrium and out-of-equilibrium platinum coordination modes can be orthogonally controlled thermodynamically with a proton input and kinetically using light.

Main text

The operational basis for devices and smart materials, such as molecular machines[1] and switchable polymers[2], is often a non-covalent (supramolecular) or transition metal-ligand motif which undergoes reversible change in response to an external stimulus. In almost all cases,[3] the stimulus functions by adjusting the thermodynamic position of the equilibrium; in systems that rely upon exclusively weak interactions such as hydrogen-bonding or π-π interactions,[1a-c] re-equilibration often occurs very quickly such that out-of-equilibrium states cannot be easily detected. In contrast, systems which utilise transition metal-ligand interactions often occur on a much slower timescale, minutes, hours or even days.[4,5] As such, metastable states, which have been shown to be important in molecular electronics[6] and machine ratcheting mechanisms[7], can be observed or even isolated and these systems often require the input of heat to overcome the kinetic barrier to re-equilibration.[5,8,9] However, heat does not alter the magnitude of this barrier and so cannot be thought of as a "kinetic stimulus". Here we report the switchable behaviour of heteroleptic, acceptor-donor-type platinum coordination complexes in which we orthogonally use a proton input to adjust the equilibrium position and exploit light to selectively lower the energetic barrier to equilibration.

The system under study aimed to combine the preference of group 10 transition metals to selectively bind heterocycles as a function a basicity,[2b,5] a thermodynamic bias that can be reversed by the addition of an equivalent of acid,[5] with the known photochemical lability of 2nd and 3rd row transition metals. While light-promoted ligand exchange is well documented for Ru(II),[10] in particular, it has recently been shown that the rates of Pt(II) substitution can also be increased upon photoirradiation.[11] In order to control the selective exchange of just a single ligand, we chose to investigate the neutral platinum motif[12] [**L**Pt(PyR)] (Scheme 1) as it was envisaged that the tridentate, doubly charged $\mathbf{L}^{2-}$ would not undergo dissociation from the platinum centre on exposure to light. Initially, the thermodynamically downhill exchange of *N,N′*-dimethylaminopyridine ($PyNMe_2$) for the pyridine ligand of [**L**Pt(PyH)] was investigated (Scheme 1a). Upon broad band 275-375 nm irradiation (with a λ_{max} of 312 nm, see Supporting information) of a 0.01 M solution of [**L**Pt(PyH)] and $PyNMe_2$ in 1:1 [D_7]DMF:CD_2Cl_2, a steady-state equilibrium of 17:83 [**L**Pt(PyH)]:[**L**Pt($PyNMe_2$)] was obtained after 10.5 h. To investigate the effect an increase in the pK_a difference of the two exchangeable heterocycles would have on both the thermodynamic bias and the rate of equilibration, the reaction of $PyNMe_2$ and [**L**Pt($PyCF_3$)] was also investigated (Scheme 1a). Under the same conditions (0.01 M, 1:1 [D_7]DMF:CD_2Cl_2) 4.5 h irradiation gave a steady-state ratio of 11:89

[**L**Pt($PyCF_3$)]:[**L**Pt($PyNMe_2$)]. In both cases, the exchange experiment was followed directly by ^{1}H NMR spectroscopy (Figure 1). To assess the effect of light, both reactions were also carried out under identical conditions (0.01 M in 1:1 [D_7]DMF:CD_2Cl_2, 313 K) but in the dark. The reaction of $PyNMe_2$ with [**L**Pt($PyCF_3$)] took 44 h to reach an equilibrium ratio of 15:85, within error of the ratio obtained under irradiative conditions,[13] indicating that light significantly lowers the activation barrier to exchange without perturbing the relative ground state energies. In the absence of light, equilibration of [**L**Pt(PyH)] with $PyNMe_2$ at the same temperature (313 K) gave a ratio of 28:72 after 11 days. However, the sluggishness of the thermal exchange process (even at 333 K), coupled with the slow but steady decomposition of the complexes that occurred after further, prolonged heating, ensured that this reaction could not be followed to completion.



Scheme 1. Dual stimuli-responsive exchange between Pt coordinated $PyNMe_2$ and PyR (R = H or CF_3) as a function of light and protons. All reactions carried out at 0.01 M in 1:1 [D_7]DMF:CD_2Cl_2 at 313 K, either in the presence or absence of light (broad band 275-375 nm). The ratios correspond to the equilibrium ratios

obtained after x h starting from (a) [**L**Pt(PyR]; (b) [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs; (c) [*cis*-H**L**Pt(PyNMe$_2$)(S)]OTs.[15] [a]Ratio taken prior to equilibration due to increasing decomposition caused by prolonged heating.[b]264 h at 313 K and then 264 h at 333 K.[15] [c]312 h at 313 K and then 264 h at 333 K.

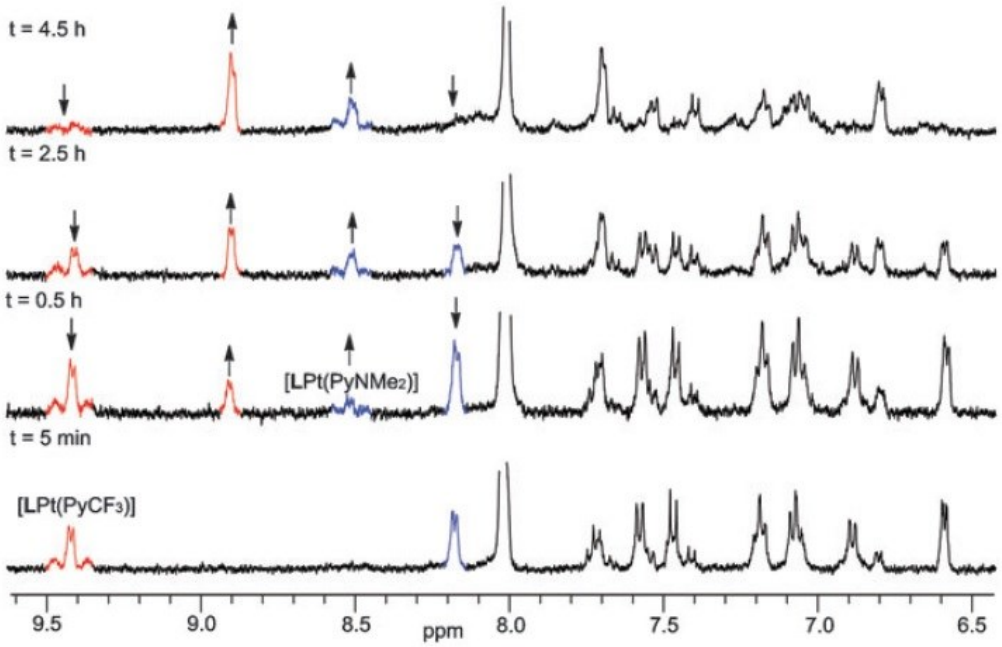


Figure 1. ^{1}H NMR spectra (400 MHz, 1:1 [D$_7$]DMF:CD$_2$Cl$_2$, 300 K) of the photochemical reaction between [**L**Pt(PyCF$_3$)] and PyNMe$_2$ over time. The *ortho* pyridyl protons of [**L**Pt(PyNMe$_2$)] and free PyNMe$_2$ are highlighted in blue and the *ortho* pyridyl protons of [**L**Pt(PyCF$_3$)] and free PyCF$_3$ in red.

The platinum-binding preference of the heterocycles cannot be reversed with just one equivalent of acid as addition of a stoichiometric amount of *para*-toluenesulfonic acid (TsOH) to a mixture of [**L**Pt(PyNMe$_2$)] and PyR (R = H or CF$_3$) results in protonation of the C^N^C complexes to give [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs (Scheme 1b).[14] Furthermore, we reasoned that the stereochemical relationship of the PyNMe$_2$ and PyR ligands with respect to the strong *trans* influence of the phenylato group of H**L**$^-$ would lead to isomers of noticeably different energy. To investigate this, [**L**Pt(PyR)] (R = H or CF$_3$) were initially treated with TsOH and then with PyNMe$_2$ to give the presumed higher energy [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs isomers. Upon light irradiation of these samples, it could be roughly observed that an increase in [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs was accompanied by a decrease in [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs (Scheme 1b). However, the complexity of these NMR spectra, caused in part by the unsymmetrical nature of the C^N complexes, prohibited a direct measure of the *cis:trans* complex ratio. Instead, an indirect measure was obtained by treating the samples, after irradiative equilibration was complete (6.5 h for R = H, 5 h for R = CF$_3$), with the base P$_1$-^{t}Bu to affect cyclometallation, from

which ratios of 26:74 (R = H) and 20:80 (R = CF_3) [**L**Pt(PyR)]:[**L**Pt(PyNMe$_2$)] could be obtained.[15] For comparison, the non-irradiative reactions produced ratios of 49:51 (R = H) and 30:70 (R = CF_3) after 11 days at 313 K and a further 11 days at 333 K. In both cases, the thermal reactions were halted prior to equilibrium due to small amounts of decomposition.

To reverse the coordinative bias of the heterocycles, it was anticipated that a second equivalent of acid could be used. Promisingly, the addition of 1 equiv. of TsOH to [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs (R = CF_3 or H) in 1:1 [D_7]DMF:CD_2Cl_2 resulted in liberation of PyR.TsOH along with formation of a complex we presume to be the solvato complex [*cis*-H**L**Pt(PyNMe$_2$)(S)]OTs, where S = [D_7]DMF. Irradiation of these solutions resulted in the emergence of PyNMe$_2$.TsOH and the concomitant reduction of PyR.TsOH (R = CF_3 or H) (Scheme 1c). However, the complexity of these NMR spectra, again, prohibited a direct measure of the equilibrium position, so the samples were treated with P_1-^{t}Bu after 5.2 h (R = H) and 5.5 h (R = CF_3) irradiation, from which ratios of [**L**Pt(PyR)]:[**L**Pt(PyNMe$_2$)] of 70:30 (R = H) and 85:15 (R = CF_3,) were obtained. Again, for comparison, the thermal reactions produced ratios of 41:59 (R = H) and 63:37 (R = CF_3) after 13 days at 313 K and a further 11 days at 333 K. Both themal reactions were again stopped prior to equilibrium due to small amounts of decomposition.

A likely mechanism for the pronounced rate enhancements upon irradiation is through excitation into a metal centred (MC) state with σ antibonding $d_{x^2-y^2}$ character.[11a,b] Due to the heavy atom effect, it is probable that this proceeds *via* a ^{3}MLCT (metal-ligand charge transfer) state, from which the ^{3}MC state is thermally accessible.[12] However, strong field cyclometallated ligands are known to raise the energy of the MC state, which is why many similar Pt complexes are luminescent, rather than photochemically active, at room temperature.[16] In this current investigation, it could be anticipated that the MC states of [**L**Pt(PyR)] would be less accessible than the corresponding states for either [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs or [*cis*-H**L**Pt(PyNMe$_2$)(S)]OTs. This appears to be supported, experimentally, as the C^N complexes exhibit greater irradiative rate enhancements in comparison to the thermal reactions (in effect, protonation photochemically activates the C^N^C complexes).[17] Interestingly, it is known that the related C^N^C complex [**L**Pt(CNPh)] is not luminescent at room temperature and a recent theoretical analysis has shown that a likely reason for this is due to significant distortion of the triplet ground state, which reduces the ligand field and brings the MC state into thermal range.[18]

In conclusion, we have described the orthogonal, dual stimuli-responsive behaviour of heteroleptic cyclometalled platinum complexes, in which protons are used to switch the thermodynamic bias, and in which light functions as a true kinetic stimulus by lowering the activation barrier to ligand exchange. We envisage that switchable complexes such as these, where both the thermodynamic and kinetic components of switching can be independently manipulated, will play a pivotal role in the development of future devices and smart materials.

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[15] The ratios of [**L**Pt(PyR)]:[**L**Pt(PyNMe$_2$)] for the reaction of [**L**Pt(PyR)] + PyNMe$_2$ →[**L**Pt(PyNMe$_2$)] + PyR were measured directly by integration of the ^{1}H NMR spectra. The ratios of [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs:[*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs and [H**L**Pt(PyR)(S)]OTs:[H**L**Pt(PyNMe$_2$)(S)]OTs were measured indirectly by converting the corresponding C^N complexes to C^N^C complexes using the base P$_1$-^{t}Bu, and then by integration of the resultant [**L**Pt(PyR)] and [**L**Pt(PyNMe$_2$)] complexes. This cyclometallation reaction is fast in comparison to the ligand exchange processes; at room temperature it is complete within the 5 minutes it takes to acquire a ^{1}H NMR spectrum. As control experiments, when samples of pure [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs and [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs are treated with P$_1$-^{t}Bu, they exclusively yield [**L**Pt(PyR)] and [**L**Pt(PyNMe$_2$)], respectively. It is possible that in addition to [*trans*-H**L**Pt(PyNMe$_2$)(PyR)]OTs and [*cis*-H**L**Pt(PyR)(PyNMe$_2$)]OTs, [H**L**Pt(PyNMe$_2$)$_2$]OTs and [H**L**Pt(PyR)$_2$]OTs are also formed during the ligand exchange process. However, mass spectrometry was ineffective in confirming this as only [H**L**Pt(PyNMe$_2$)]$^{+}$ and [H**L**Pt(PyR)]$^{+}$ could be detected, due, it is presumed, to the relatively weak coordination of the heterocycle *trans* to the phenylato group of H**L**.

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